Characterization And Ionic Conductivity Of Polymeric Electrolytes Based On Chitosan-Ammonium Thiocyanate-TiO_2 Ceramic Materials

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Abstract

Various amounts of TiO_2 particles are used as filler in preparation of chitosan-ammoniu thiocyanate-composite polymer electrolytes. The role of filler in this present work is as agent to improve the conductivity of the films. Films of chitosan and its complexes we prepared using solution casting technique. Different amounts of TiO_2 3 wt. %, 6 wt. %, 9 w %, 12 wt. %, 15 wt. % and 18 wt. % were added to the highest room temperature conducti sample in chitosan-salt system i.e sample containing 40 wt. % NH_4SCN. The impedance the composite films has been measured in the temperature and the frequency range 298 K 373 K and 50 Hz to 1 MHz, respectively. The conductivity value of this sample is 1.29 x 1 S cm^{-1}. With addition of 3 wt. % TiO_2 filler the ionic conductivity increased to 2.75 x 10^{-4} cm^{-1}. XRD and FTIR results are also disscused.

Keywords: ionic conductivity, ceramic fillers, polymer-nanocomposite, chitosan

1. INTRODUCTION

Solid polymer electrolytes have been the subject of numerous studies. Their technological importance can be seen in the fabrication of lithium-ion polymer batteries [1], capacitors [2], and electrochromic devices [3]. Most research on electrolytes focused on increasing their conductivity while at the same time maintains good thermal and mechanical stability. The addition of inert oxides to the polymer electrolytes has recently become an attractive approach, due to improved mechanical stability and enhanced ionic conductivity [4-6]. The increase in conductivitfy of the composite electrolytes depends upon the concentration and the sizes particle fillers. In general, the smaller the inert particle, the larger the conductivity enhancement [7-8].

The disadvantage of organic fillers such as propylene carbonate (PC) and ethylene carbonate (EC) is that they are mo expensive compared with inorganic fille [9]. Fillers can promote more free ions a produce more amorphous regions in t electrolyte for transport of charge carrie [10].

In this work chitosan-NH_4SCN-Ti composite polymer electrolyte has be developed, in which the titanium dioxi (TiO_2) as the filler has increase t conductivity. The effects of TiO_2 chitosan-NH_4SCN are also studied by XR FTIR and SEM.

2. EXPERIMENTAL

2.1 Materials and Preparation

Chitosan (highly viscous) was procur from Fluka as the polymer host. Acetic ac was procured from Univar Chemica Ammonium thiocyanate (R&M) was used

the doping salt and TiO_2 (titanium (IV) oxide) from Aldrich was used as filler.

The chitosan was dissolved in 1 % acetic acid and the mixture was stirred at room temperature for 3 h to obtain a homogeneous solution. 40 wt. % of ammonium thiocyanate was added to the solution and stirred until the salt has dissolved completely. TiO_2 was added accordingly at the required concentrations. The homogenous solution was then cast into several plastic petri dishes to get the films.

2.2 Characterizations

2.2.1 Conductivity Measurements.

The dried films were cut into a suitable size and mounted on the conductivity holder with stainless steel electrodes of 1 cm diameter under spring pressure. The impedance of all samples was measured using the HIOKI 3531-01 LCR Hi-Tester interfaced to a computer with frequency ranging from 50 Hz to 1 MHz and also at temperatures from 298 K to 393 K. The electrical conductivity was then calculated using the equation:

$$\sigma = \frac{t}{R_b A} \qquad (1)$$

Here t is thickness of the sample, A is the surface area of contact and R_b is the bulk resistance of the sample.

2.2.2 X-Ray Diffractometer (XRD)

X-ray diffraction was performed using Shimadzu D5000 to examine the crystalline nature of the prepared polymer composite samples.

2.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy patterns were recorded using Thermo Scientific/Nicolet iS10. Infrared absorption spectra were collected in the range from 4000 to 400 cm^{-1} at room temperature with a resolution of 1 cm^{-1}.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of some prepared samples obtained at room temperature.

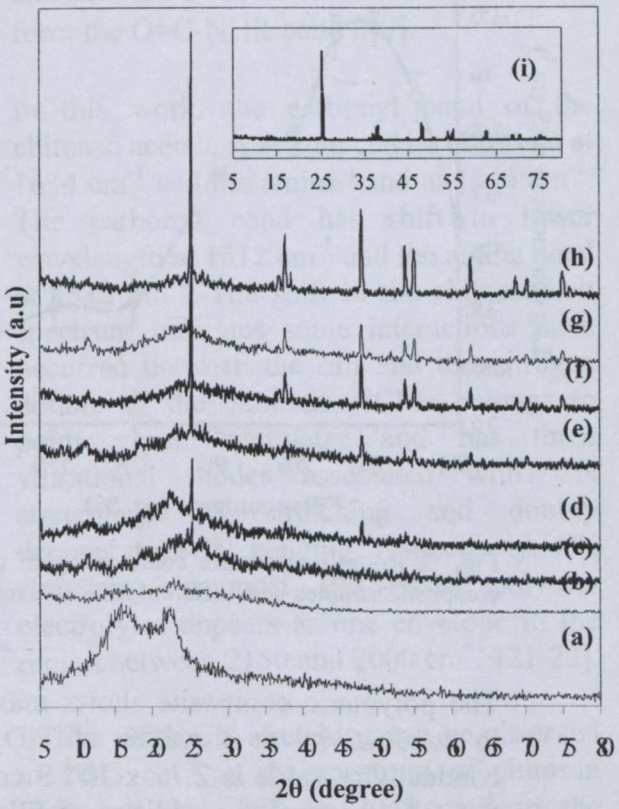

Fig. 1 Diffractograms of films for (a) pure chitosan acetate, (b) chitosan acetate-40 wt. % NH_4SCN, (c) chitosan acetate - 40 wt. % NH_4SCN - 3 wt. % TiO_2, (d) chitosan acetate-40 wt. % NH_4SCN - 6 wt. % TiO_2, (e) chitosan acetate-40 wt. % NH_4SCN- 9 wt.% TiO_2, (f) chitosan acetate-40 wt. % NH_4SCN - 12 wt. % TiO_2, (g) chitosan acetate-40 wt. % NH_4SCN - 15 wt.% TiO_2, (h) chitosan acetate - 40 wt. % NH_4SCN - 18 wt.% TiO_2 and (i) pure TiO_2.

The XRD pattern of pure chitosan shows two halos at $2\theta=15.5^{\circ}$ and 21.6°. It was reported that pure chitosan film exhibit peaks at 2θ angles of 21°, between 16° to 24° and 29° [11]. When 40 wt. % NH_4SCN was added to pure chitosan acetate, the intensity of both peaks has decreased and gives a completely amorphous film. The broad peaks indicate that the films are amorphous [12]. The conductivity will increase when the material becomes more amorphous or less crystalline. Based on the diffractograms, the sample with 3 wt. % of

filler exhibits the most amorphous diffractogram. Thus it may have higher conductivity compared to the other samples. Fig. 2 shows the effect of filler on the conductivity of chitosan-NH_4SCN-TiO_2 system at room temperature.

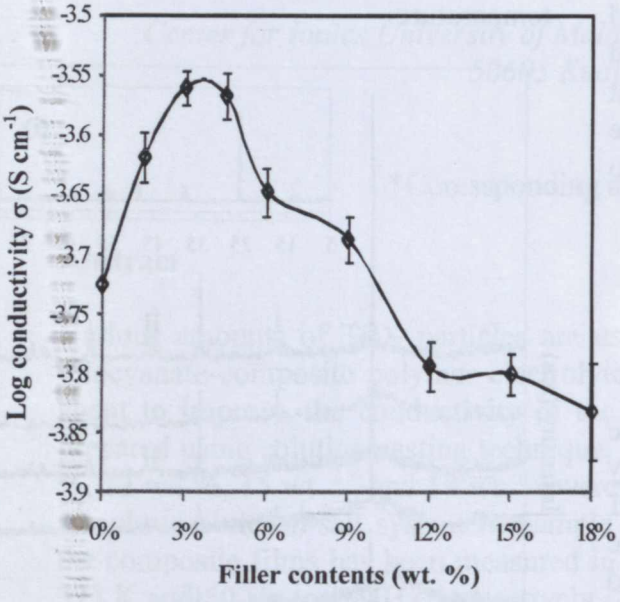

Fig. 2 Room temperature conductivity of polymer composite samples with different filler content.

The polymeric composite shows maximum in conductivity at 3 wt. % of TiO_2. The conductivity value is 2.75 x 10^{-4} S cm^{-1}. At this filler content, the addition of filler may have created additional pathways for the ion to transport and could have also resulted in a greater number of mobile ions due to dissociation of the salt. [13-14]. The conductivity decreases for the sample containing 6 wt. %, 9 wt. %, 12 wt. %, 15 wt. % and 18 wt. %. This results are in good agreement with the XRD results where the crystallinity of the samples have increased with increasing amount of filler thus decreasing the conductivity. The conductivity (σ)-temperature (T) plots of the chitosan based electrolyte is shown in Fig. 3.

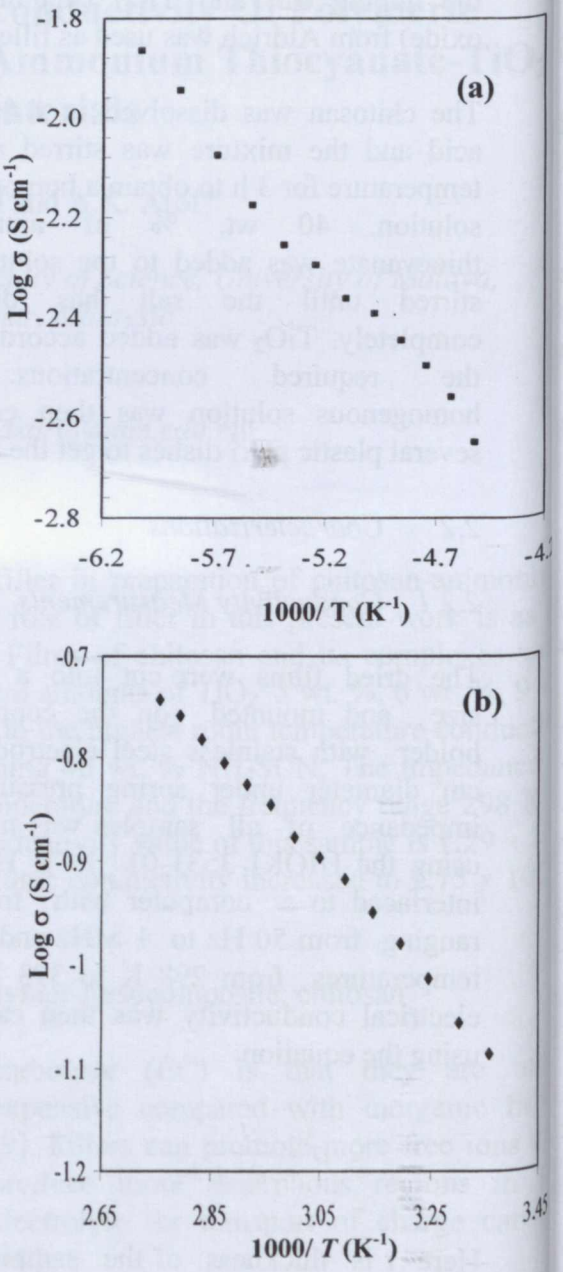

Fig. 3 Arrhenius plot of conductivity for (a) chitos acetate-40 wt. % NH_4SCN and (b) chitosan aceta 40 wt. % NH_4SCN-3 wt.% TiO_2.

The plot shows that as the temperatu increases, the conductivity also increase Ng and Mohamed [15] have also observe the same trend. The conductivit temperature relationship of chitosan-bas polymer electrolyte can be characterized Arrhenius behavior, suggesting th conductivity is thermally stable. T activation energy, E_a of the sample can calculated using the modified Arrheni equation below:

$$\sigma = \sigma_o \exp(E_a / K_B T) \quad (2$$

Here T is the experimental temperature in Kelvin, σ is conductivity, σ_o is pre-exponential factor, E_a is the activation energy and K_B is the Boltzmann constant. From the slope of the graph in Fig. 3, the calculated activation energy for conduction is 0.19 eV and 0.08 eV for salted and composite samples, respectively. The decrease in activation energy is consistent with an increase in conductivity as reported in many reports on conductivity studies of polymer electrolytes [16-17].

The increase in ion dissociation and reduction of ion pairing in the electrolyte can be discussed further based on the FTIR spectrum as shown in Fig. 4.

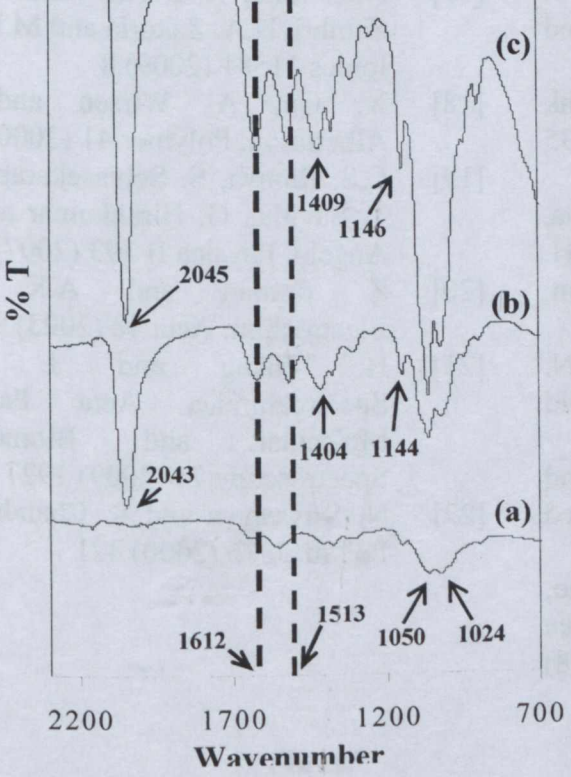

Fig. 4 IR spectrum of film containing (a) chitosan acetate, (b) chitosan acetate-NH_4SCN and (c) chitosan acetate-NH_4SCN-TiO_2 in the region from 700 to 2300 cm^{-1}

Fig. 4 depicts the spectra of pure chitosan, chitosan acetate with salt and chitosan acetate with salt and filler. The carbonyl (C=O-NHR), amine (NH_2) and ammonium (NH_3^+) bands are situated in the region between 1400 and 1700 cm^{-1}. From the literature, the C=O-NHR band can be observed at 1650 cm^{-1} [18], the amine NH_2 band is at 1590 cm^{-1} and the ammonium NH_3^+ band at 1514 cm^{-1} [19]. Sometimes, the absence of the NH_3^+ pure chitosan acetate spectrum is probably due to the interaction between NH_3^+ of the chitosan and the -COO- of the acetic acid solvent to form the O=C-NHR band [20].

In this work, the carbonyl band of the chitosan acetate spectrum can be observed at 1634 cm^{-1} and the amine band at 1544 cm^{-1}. The carbonyl band has shift to lower wavelength at 1612 cm^{-1} and the amine band at 1513 cm^{-1}. The shift in the chitosan-salt spectrum indicates some interactions have occurred between the salt and the nitrogen donors of the chitosan. SCN^- belongs to point group symmetry and has three vibrational modes associated with CN stretching, CS stretching and doubly degenerate SCN bending, respectively. CN stretching in most PEO-based polymer electrolytes appears as one envelope in the region between 2150 and 2000 cm^{-1} [21-22].

In this work CN stretching can be observed at 2043 cm^{-1} in the spectrum of chitosan with salt and shift to 2045 cm^{-1} in the spectrum of chitosan with salt and filler. The intensity of this band also increases due to the addition of filler. The polymer–salt complex formation and the proton interaction have been confirmed from the above analysis.

4. CONCLUSIONS

It can be inferred that the presence of the ceramic filler can help to improve the conductivity of the prepared samples. XRD and FTIR results clearly showed interaction between TiO_2 filler and the completely amorphous chitosan-based polymer electrolyte. The conductivity value of the order ~10^{-4} S cm^{-1} that has been obtained by adding the TiO_2 filler to chitosan-salt polymer electrolyte can make the composite polymer electrolyte as a potential material for some electrochemical devices.

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